

Chapter 23

Characterization of Hydrophilic and Hydrophobic Ionic Liquids: Alternatives to Volatile Organic Compounds for Liquid-Liquid Separations

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Herein we describe the physical and chemical properties for several Ionic Liquids (ILs) comprised of the 1-alkyl-3-methylimidazolium cation with the Cl^- , Br^- , I^- , BF_4^- , or PF_6^- anions. Liquid-liquid separations with the PF_6^- ILs are highlighted to illustrate their use in "Green Chemistry," as alternatives to traditional organic solvents in separations. The partitioning of organic molecules, combined with IL characterization, has facilitated successful metal ion extraction with both anionic and molecular extractants. This report discusses our current results in the characterization of ILs, their use in liquid-liquid extraction, new concepts for metal ion separations, and solid-state analyses.

Introduction

The curiosity surrounding Ionic Liquids (ILs) has focused on their unique properties, particularly as alternatives to traditional organic solvents in synthesis (1) and in liquid-liquid separations from aqueous solutions (2-6). Separation

processes employing liquid-liquid extractions are a common industrial unit operation, the characteristics of the extracting phase can be fine tuned by selection from the many organic solvents available (7). However, most common solvents are volatile organic compounds (VOCs), and their associated chemical behavior (in addition to their potential toxicity) classifies many of them as hazardous substances.

Green Chemistry

Early social perceptions of chemistry and the chemical industry centered on innovations in medicine, technology, and the overall improvement in the quality of life. More recently, with the rapidly expanding chemical industry, those perceptions have changed and many perceive the industry as a major contributor towards air, land, and water pollution. Each year, the U.S. produces millions of tons of pollution and, at the same time, spends tens of billions of dollars controlling this pollution in the production and cleanup cycle. Therein is the indication that redesigning of chemical production processes may be more effective through targeting source reduction instead of "end of the pipe" waste management or pollution control (8). Ideally, pollution would be controlled or minimized at the source, recycling would be done if possible, and any unavoidable waste production would be handled in an appropriate manner.

The chemical industry realizes that their sustained future growth, revenue, and scientific development may depend on considering how their production practices and technologies impact the health and safety of their employees and the environment. Major laws, such as the Clean Air Act and Pollution Prevention Act, have been the impetus for many of these changes (8).

Subsequently, the idea of "Green Chemistry" was established to promote the research, development, and implementation of innovative chemical technologies to achieve pollution prevention in a technologically and economically sound manner (8). All this would be achieved, from the green chemistry standpoint, through technologies that reduce the consumption or production of hazardous chemicals during the manufacturing or processing of chemical products. A decrease in the generation of hazardous chemicals, along with a diminished potential for health and environmental problems, would be the direct result of a new paradigm for chemical manufacturing or processing.

New Solvent Technologies

Many chemicals that are routinely used are a necessary part of the manufacturing process and yet dangerous to health and the environment. The penchant for traditional solvent extraction systems has come to a crossroads as

the emphasis for sustainable technology and green chemistry considers the overall environmental impact of both the process and waste streams generated as a result.

We have been investigating ILs and polymer-based Aqueous Biphasic Systems (ABS) as alternatives to traditional organic solvents in liquid-liquid separations. Although both areas have their own specialized literature, several reports highlight separations based on ILs (3,10-12) or ABS (13-15) where the merits of both systems show their potential for implementation into industrial separations systems. Most notable from a "Green" perspective is the fact that both ABS and ILs can be used in place of VOCs in liquid-liquid separations. Other work on novel solvent media has shown how supercritical water (16,17), supercritical CO₂ (9), solventless phases (18), and fluoruous phases (19) can be used in an effort to broaden the scope of possibilities available for more environmentally responsible processes.

Room Temperature Ionic Liquids (RTILs)

RTILs (or, more generally, ILs), as discussed in this book, are a class of novel compounds composed entirely of ions that, together, melt at or below ambient temperatures (or below 150 °C for ILs) and may be thought to resemble molten ionic melts such as NaCl at 800 °C. While both ILs and molten salts are composed of ions, the presence of organic cations in ILs interrupts the crystal packing and lowers the melting point. Depending on the composition, the resulting IL can be hydrophobic or hydrophilic. An inherent property of many ILs is their miniscule volatility and easily manipulated properties, characteristics of a unique class of solvents. Literature reports are awash with cations for use in these systems, including ammonium (20-22), pyridinium (23,24), pyrrolidinium (25), isoquinolinium (26), and imidazolium (2,27), each with the possibility for attaching various alkyl groups to the ring or quaternary onium cation. Depending on the type of cation investigated and the length of the alkyl chain, the resulting salts may have a melting point above room temperature and several crystal structures have been reported (28).

In our research, we have focused on RTILs incorporating the 1-alkyl-3-methylimidazolium ([C_nmim]⁺) cation, as shown in Figure 1 (2-4). The alkyl group is usually an *n*-alkane and increasing the length of the alkane chain affects the resulting properties (e.g., viscosity, hydrophobicity, and melting point (2,27)). For example, [C₈mim][PF₆] is a liquid at room temperature with a glass transition temperature at -75 °C (2) and [C₁₀mim][PF₆] melts at 38 °C (3). RTILs composed of several different cations or anions (i.e., multi-component mixtures) can be envisaged to further expand the family of ionic liquids.

IL cations and anions can be used to control the water miscibility of the resulting ILs and the choice of anion has been used to the greatest effect on

controlling hydrophobicity. 1-alkyl-3-methylimidazolium salts of PF_6^- are water immiscible, BF_4^- salts are water miscible depending on alkyl chain length, and tetrahaloaluminate salts are moisture sensitive. Fluorinated anions such as $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ impart even greater hydrophobicity despite increased expense (27).

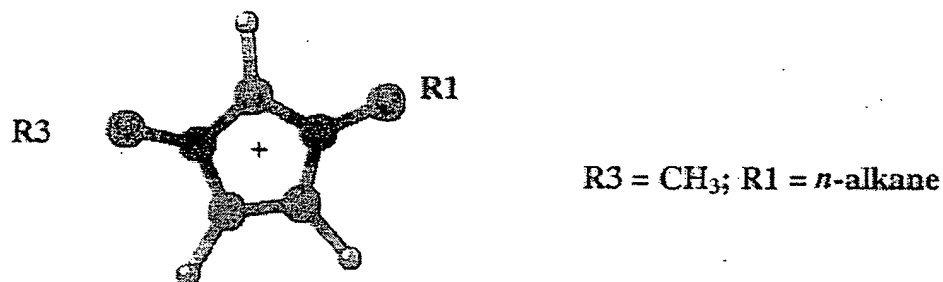


Figure 1. Generic cations for 1-alkyl-3-methylimidazolium RTILs.

The ionic liquids we have used in our liquid-liquid studies are all liquids below 40 °C, although 150 °C is the adopted upper temperature limit for 'ionic liquid' classification. RTIL is an arbitrary subdivision of ILs that are liquid at room temperature and, thus, facilitate their use at ambient temperatures. Here, we will provide an overview of organic partitioning and metal ion extraction in RTIL-aqueous systems with particular focus on the effects of anion selectivity, increasing alkyl chain length, and cation substitution.

Experimental

The experimental details for the data and procedures reported here are provided in references to physical properties (2), organic solute partitioning (29), and metal ion extraction (4-6). Distribution ratios as reported here are defined as the ratio of the solute concentration in the RTIL lower phase divided by the solute concentration in the aqueous upper phase.

Thymol blue (3) partitioning was measured via UV-Vis spectroscopy while the remaining organic solute and metal ion studies reported here utilized radio-labeled chemicals. The methods for chemical and physical characterization of the ILs are described elsewhere (2).

Results

Partitioning of Organic Solutes

Our initial results (29) for aromatic solute partitioning between water and $[C_4mim][PF_6]$ indicated that neutral, hydrophobic, aromatic solutes have an affinity for the ionic liquid phase, as shown in Figure 2. For the simple benzene derivatives investigated, partitioning to the RTIL phase generally increased in accordance with the solutes' 1-octanol-water log P values, a common measure of solute hydrophobicity. This demonstrated that partitioning could be achieved and, in many cases, partitioning can be predicted (and/or modeled) using traditional solvent extraction parameters. In this manner, ILs behaved as conventional solvents, displaying a noticeable affinity for aromatic solutes and low aliphatic solubility. Once in the RTIL phase, volatile organic solutes can be removed by distillation or pervaporation, as the RTILs themselves may have negligible vapor pressure. Many non-volatiles can be removed through contact with supercritical CO_2 (9). The solubility of $[C_nmim][PF_6]$ in various ethanol-water solutions (30) suggests complex solution behavior with increasing mole fractions of traditional solvents.

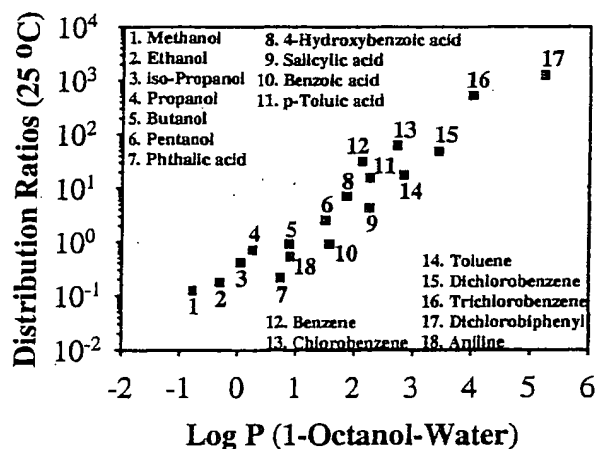


Figure 2. Distribution ratios of organic solutes for the $[C_4mim][PF_6]$ -water biphasic system; data from ref. (29).

With charged or ionizable solutes, a change in the aqueous phase pH resulted in certain ionizable solutes exhibiting pH-dependent partitioning such that their affinity for the RTILs decreased upon ionization (29). As shown in Figure 3, solute ionization affects the partitioning of aniline and benzoic acid and may be sufficient to cause several orders of magnitude difference in the

partitioning. Thus, for ionizable solutes, a change in aqueous phase pH could be used for solute recovery from the RTIL phase.

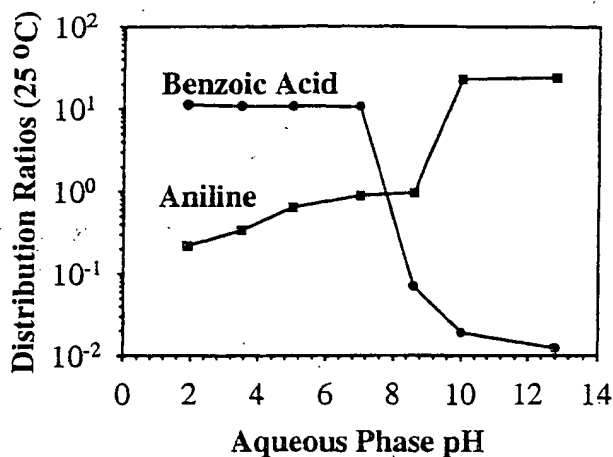


Figure 3. Distribution ratios for aniline ($pK_b = 9.42$) and benzoic acid ($pK_a = 4.19$) in $[C_4mim][PF_6]$ -aqueous systems as a function of aqueous phase pH.

Other solutes may have substituent groups that hinder their solubility and partitioning in RTIL-water systems. We have studied the partitioning of unsubstituted, *t*-butyl-, and sulfonated-calixarenes in a series of $[C_nmim][PF_6]$ -water systems as a function of aqueous phase pH (31). The hydrophobic nature of the RTILs offers an environment suitable for solubilizing the unsubstituted calix-4 and calix-6-arenes, where distribution ratios for both molecules are above 100 and are relatively unaffected by aqueous phase pH. However, the *t*-butyl-calixarenes were not soluble in these RTILs. Adding sulfonate groups to the calixarenes diminished their affinity for the RTIL phase and distribution ratios indicate those molecules prefer the aqueous phase.

We further investigated the pH dependent partitioning of the cationic dye, thymol blue, in these systems (3). As depicted in Figure 4, thymol blue preferred the RTIL phase in both the zwitterionic and monoanionic form and partitioned to the aqueous phase under basic conditions. Of the RTILs investigated in liquid-liquid partitioning experiments, thymol blue distribution ratios increased with RTIL hydrophobicity (or lipophilicity) and were highest in $[C_8mim][PF_6]$. Solid-liquid separations were performed with $[C_{10}mim][PF_6]$ to illustrate how successive heating, mixing, and cooling, combined with appropriate pH changes, could remove thymol blue from an aqueous phase with no retention of the dye upon recrystallization of $[C_{10}mim][PF_6]$ (3).

The behavior of organic solutes in RTIL systems illustrates both the unique and unexpected characteristics of RTIL-based separations. With respect to organic solutes, traditional descriptors provide a good indication of solute

affinity for the RTIL phase. For ionizable molecules, ionization has an apparent effect on phase affinity and may provide a facilitated means for stripping. When selecting or modifying a RTIL, the resulting hydrophobicity has a significant impact on partitioning results.

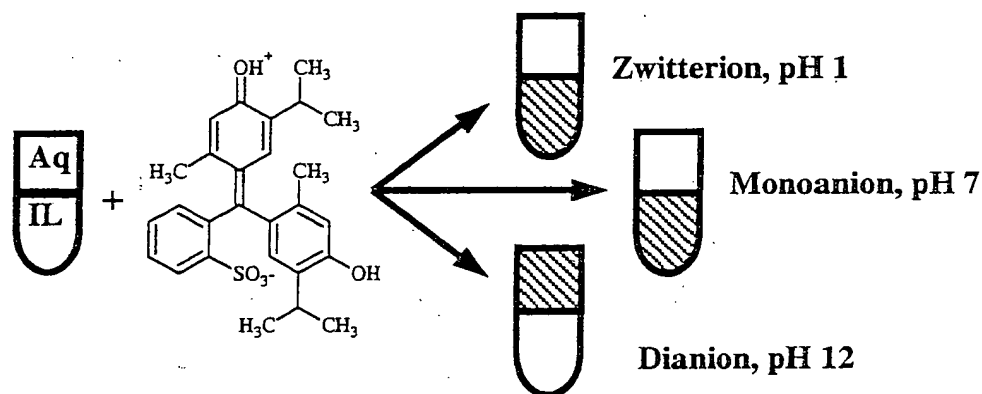


Figure 4. Behavior of thymol blue in $[C_n\text{mim}][PF_6]$ -aqueous biphasic systems as a function of aqueous phase pH (3).

Metal Ion Extraction

In liquid-liquid separation systems, the hydrated nature of most metal ions lowers their affinity for the extracting phase. This is the case in RTIL systems where hydrated metal ions do not partition to ILs from water (5,32). Therefore, it is necessary to change the hydration environment of the metal ion by either using organic ligands (33-35) which provide a more hydrophobic region around the metal or form neutral compounds, or with inorganic anions (36) that form softer more extractable anionic complexes with the metal. Ideally, in a biphasic system, the extractant would remain in the hydrophobic phase to ensure the complete removal of the metal ions from the aqueous phase. Thus, the challenges in adapting new classes of solvents to traditional separations include finding extractants which quantitatively partition to the solvent phase and can still readily complex target metal ions; or finding conditions under which specific metal ion species can be selectively extracted from aqueous streams containing inorganic complexing ions.

Organic Extractants

Our initial studies used 1-(2-pyridylazo)-naphthol (PAN) and 1-(2-thiazolyl)-2-naphthol (TAN) as extractants for metal ions in light of their success in

polymer-based ABS (37) and traditional solvent extraction systems (38). These are conventional metal extractants widely used in solvent extraction applications. When the aqueous phase is basic, both molecules are ionized, yet they quantitatively partition to $[C_6\text{mim}][PF_6]$ over the pH range 1-13. As other reports indicate (39), the ionization of the molecules plays an important role in the metal ion extraction, as shown in Figure 5. The distribution ratios for Fe^{3+} , Co^{2+} , and Cd^{2+} show that metal ions could be extracted from the aqueous phase at basic pH and stripped from the RTIL under acidic conditions.

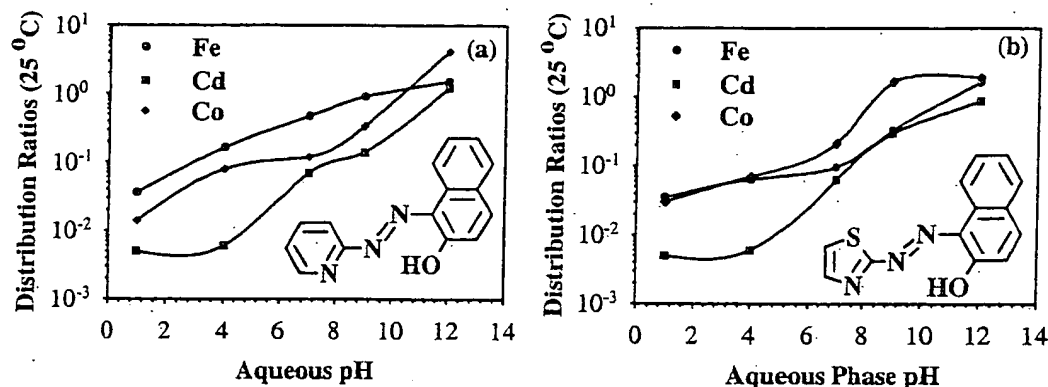


Figure 5. Metal ion distribution ratios with 0.1 mM PAN (a) or TAN (b) in $[C_6\text{mim}][PF_6]$ -aqueous systems as a function of aqueous phase pH (37).

Macrocyclic ligands such as crown ethers have been widely used for metal ion extraction (35,40). The structure and cavity size of the crown ether is the basis for metal ion selectivity and by attaching alkyl or aromatic ligands to the crown, the hydrophobicity of the ligand can be adjusted. Others have used dicyclohexano-18-crown-6 as an extractant for Sr^{2+} in $[C_n\text{mim}][N(SO_2CF_3)_2]$ RTIL liquid-liquid systems with impressive results (11). However, the conditions for optimal extraction in the RTIL system (i.e., low HNO_3 concentrations) were unexpected and contrary to what is typically employed in solvent extraction (40). We have used 18-crown-6, dicyclohexano-18-crown-6, and 4,4'-(5')-di-(*t*-butylcyclohexano)-18-crown-6 as extractants for Sr^{2+} , Cs^+ , and Na^+ in $[C_n\text{mim}][PF_6]$ -aqueous systems (4). Our results for the partitioning from HNO_3 are contrary to traditional solvent extraction behavior in that while the most hydrophobic extracting phase usually produces the highest distribution ratios, as expected, distribution ratios decrease with increasing acid concentrations.

It was noted, however, that in the presence of increasing HNO_3 (i.e., 1 - 8 M), the degradation of PF_6^- to PO_4^{3-} significantly increased the hydrophilicity of the RTIL phase and produced a monophasic system. Using $Al(NO_3)_3$ as the

source of the nitrate anion leads to an increase in distribution ratios (Figure 6) and precluded the degradation of PF_6^- observed at high concentrations of HNO_3 . Our results indicate that metal ion partitioning is very complex in RTIL-based liquid-liquid systems and other factors such as aqueous phase composition and water content of the RTILs have dramatic effects on both the metal ion extraction and the stability of the RTILs.

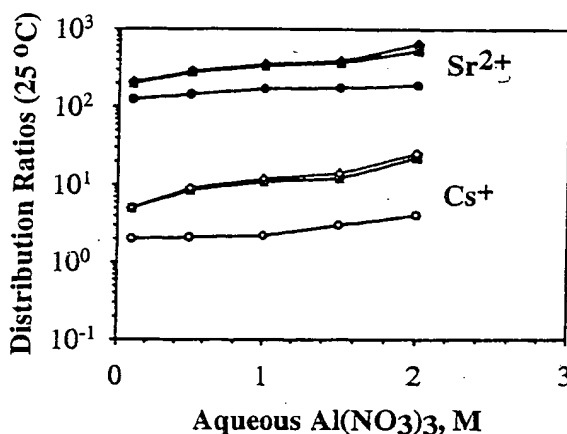


Figure 6. Sr^{2+} and Cs^+ distribution ratios with 0.1 M di-*tert*butyl-dicyclohexano-18-crown-6 in $[\text{C}_n\text{mim}][\text{PF}_6]$ -aqueous systems ($[\text{C}_4\text{mim}]^+$ (●), $[\text{C}_8\text{mim}]^+$ (■), $[\text{C}_{18}\text{mim}]^+$ (◆) with increasing aqueous phase concentrations of $\text{Al}(\text{NO}_3)_3$ (4).

Anionic Extractants

The distribution ratios of certain metal ions may be enhanced in the presence of complexing anions such as halides or pseudohalides. Metal ions such as Hg^{2+} have large formation constants with halides (41) and their effect has been observed on the partitioning of Hg^{2+} in other systems (42). We have used halides, cyanate, cyanide, and thiocyanate as anionic extractants for metal ion partitioning in $[\text{C}_4\text{mim}][\text{PF}_6]$ -aqueous systems (5) and the results are shown in Figure 7. For the halides, the formation constants for the series of Hg-I complexes are the highest and decrease to those for Hg-F (41). That, in combination with the relative hydrophobicity of the complexes, explains why the iodide complexes produce the highest distribution ratios. The results with the pseudohalides, however, suggest a more complex partitioning mechanism since the Hg-CN complexes have the highest formation constants (41), yet display the lowest distribution ratios, similar to data found in other separations systems (42).

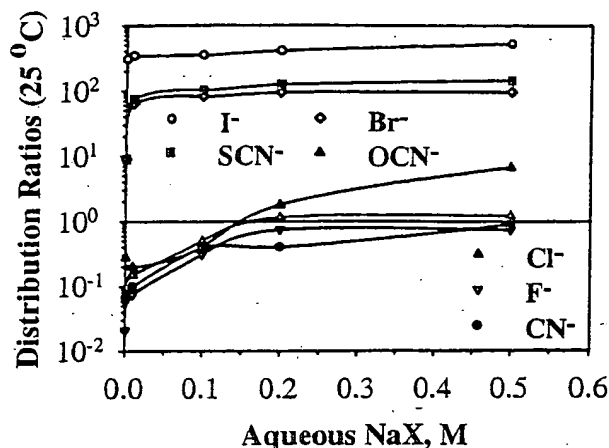


Figure 7. Hg^{2+} distribution ratios with increasing aqueous halide or pseudohalide concentrations in $[\text{C}_4\text{mim}][\text{PF}_6]$ -aqueous systems (5).

Task Specific Ionic Liquids

Through a collaboration with the Davis Group at the University of South Alabama, Task Specific Ionic Liquids (TSILs) have been utilized for metal ion separations. Here, known metal ion ligating groups are incorporated into the cationic moiety of the IL by tethering to the imidazolium cation (Figure 8).

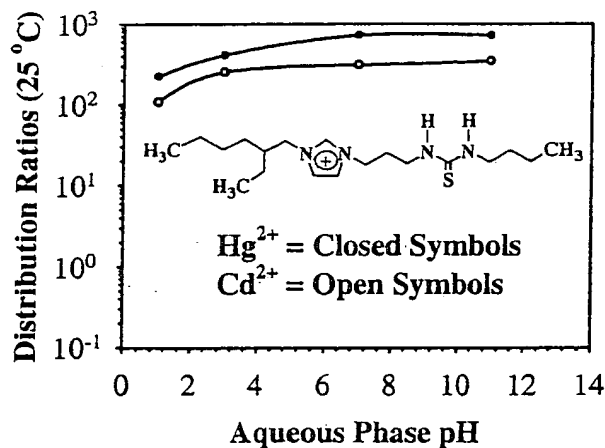


Figure 8. Hg^{2+} and Cd^{2+} distribution ratios from water to RTIL phases comprised of 1:1 combinations of $[\text{C}_4\text{mim}][\text{PF}_6]$ and a TSIL (6).

We have used thioether, urea, and thiourea derivatized imidazolium cations in conjunction with PF_6^- for the extraction of Hg^{2+} and Cd^{2+} (6). As shown in Figure 8, distribution ratios are typically higher for Hg^{2+} and a change in the

aqueous phase pH has a slight effect on the partitioning. (Thus, alternate routes may be necessary for significant metal ion stripping.) Depending on the properties of a specific TSIL, it can be used as the extracting phase or, if the TSIL melts above room temperature, in a combination with $[C_4mim][PF_6]$ as the extracting phase (6).

Physical Properties

Utilization of RTILs in solvent extraction technologies requires detailed knowledge of the solvents' physical properties (e.g., hydrophobicity, viscosity, density, surface tension, etc.). Both hydrophobic and hydrophilic RTILs have their niche, although each type may be uniquely suited for certain applications including synthesis, catalysis (43), and separations. We have utilized RTILs incorporating either the PF_6^- , $N(SO_2CF_3)_2^-$, and $N(SO_2CF_2CF_3)_2^-$ ([BETI]) anions to produce hydrophobic RTILs suitable for use in place of organic solvents for separations (2). (It should be noted that certain combinations (though not all) of imidazolium and pyridinium cations and $N(SO_2CF_3)_2^-$, $N(SO_2CF_2CF_3)_2^-$, and other hydrophobic anions are covered by U. S. Patent 5,827,602 (44).)

Solvent choice can have a substantial effect on the reaction conditions since parameters such as solvent polarity, density, and viscosity impact not only the solute environment, but also the associated engineering considerations. With traditional organic solvents, associated properties include high solute capacity, solute compatibility, and fine-tunability, although it is their volatile nature that has raised the most concern and initiated the search for solvent alternatives.

Table I is a summary of the properties for water-equilibrated [1-alkyl-3-methylimidazolium] $[PF_6]$ RTILs, as employed in many of our liquid-liquid experiments. Our previous results (2) indicate water content has a profound effect on certain properties and, in liquid-liquid separation systems analyses after equilibration with water provide the most accurate data needed for engineering RTIL processes under those conditions. The data in Table I is representative for hydrophobic RTILs in comparison to the corresponding hydrophilic RTILs listed in Tables II and III.

Despite the fact that RTILs incorporating the PF_6^- anion sustain biphasic systems, after contact with water they contain a significant, albeit non-stoichiometric, amount of water. We have shown that, for example, the water content for $[C_4mim][PF_6]$ decreases to 590 ppm after a period of drying (2), although the resulting $[C_4mim][PF_6]$ is hygroscopic and rapidly adsorbs atmospheric water to return to the saturation point. The RTILs can be successively dried by heating under vacuum. Previous partitioning results show that an increase in the alkyl chain length produces higher distribution ratios (3) for hydrophobic solutes, confirming the increase in RTIL hydrophobicity and lipophilicity.

Table I. Properties of Water-Equilibrated $[C_n\text{mim}][\text{PF}_6]$ RTILs (2)

<i>Parameter</i>	$[C_4\text{mim}]$ $[\text{PF}_6]$	$[C_6\text{mim}]$ $[\text{PF}_6]$	$[C_8\text{mim}]$ $[\text{PF}_6]$
Water content (ppm)	11700	8837	6666
Viscosity (cP, 25 °C)	397	452	506
Density (g/mL)	1.35	1.24	1.16
Melting point (°C)	4	na ^a	na
Glass transition temperature (°C)	-86	-75	-75
Thermal decomposition (°C, onset)	360	390	374
Surface tension (dyn/cm)	49.8	36.8	34.2

^a na = transition not observed.

$[C_n\text{mim}]^+$ ($n \leq 4$) combined with halides or BF_4^- (45) produce hydrophilic ILs that have subtly different properties, as shown in Tables II and III, respectively. In reality, a switch from hydrophilic to hydrophobic RTILs is a continuum that can be modified by changes in anion type and cation substitution. Other cation types, for example PR_4^+ , offer alternatives, especially lipophilic, hydrophobic systems which have densities less than 1 which could be used in conventional solvent extraction flotation systems. In Tables II and III, it is important to consider that these RTILs were characterized after being 'dried' for 4 – 5 h at 70 °C under reduced pressure.

Table II. Properties of Dried^a Hydrophilic $[C_n\text{mim}][\text{Cl}]$ ILs (2)

<i>Parameter</i>	$[C_4\text{mim}]$ $[\text{Cl}]$	$[C_6\text{mim}]$ $[\text{Cl}]$	$[C_8\text{mim}]$ $[\text{Cl}]$
Water content (ppm)	2200	1130	890
Viscosity (cP, 25 °C)		716	337
Density (g/mL)	1.08	1.03	1.00
Melting point (°C)	41	na	na
Glass transition temperature (°C)	na	-75	-87
Thermal decomposition (°C, onset)	254	253	243
Surface tension (dyn/cm)		42.5	33.8

^a dried = heating to 70 °C for 4 – 5 h while stirring, under reduced pressure.

The properties in Tables I-III confirm that compromises may be necessary when selecting an optimal IL for a particular application. Although many cation and anion combinations are available, it is evident that concessions must be made between hydrophobicity, viscosity, expense, etc. The majority of these anions are non-coordinating, although the relatively high melting point for

$[\text{C}_4\text{mim}][\text{Cl}]$ suggests that the cation-anion interactions facilitate hydrogen bonding.

Table III. Properties of Dried^a Hydrophilic $[\text{C}_4\text{mim}][\text{BF}_4]$ and $[\text{C}_4\text{mim}][\text{I}]$ ILs (2)

<i>Parameter</i>	<i>$[\text{C}_4\text{mim}][\text{BF}_4]$</i>	<i>$[\text{C}_4\text{mim}][\text{I}]$</i>
Water content (ppm)	4530	1870
Viscosity (cP, 25 °C)	219	1110
Density (g/mL)	1.12	1.44
Glass transition temperature (°C)	-97	na
Thermal decomposition (°C, onset)	403	265
Surface tension (dyn/cm)	46.6	54.7

^a dried = heating to 70 °C for 4 – 5 h while stirring, under reduced pressure.

In general, rheological properties of the RTILs vary with water content. For example, increasing the water content usually reduces viscosity. For $[\text{C}_8\text{mim}]^+$, the longer alkyl chain produces a more viscous RTIL while $[\text{C}_4\text{mim}]^+$, by contrast, has the lowest viscosity. Small amounts of chloride remaining from the synthesis may also act to increase the viscosity (46).

Density in the ILs described here decreases as the size of the cation increases since the mass of CH_2 is less than that for an imidazolium ring. In addition, as the cation size increases, surface tension decreases which can be attributed to greater charge dispersion over the cation and the associated effect on the cation-anion interactions. Ordinarily, these properties would be expected to change in a similar manner; increasing the cation size would increase both the viscosity and surface tension. Thus, viscosity and surface tension, both parameters that are highly dependent on intermolecular interactions, appear to be determined by different interactions in the ILs.

Thermal properties such as glass transition temperatures and the onset of thermal decomposition are essentially independent of the composition for these $[\text{C}_n\text{mim}][\text{PF}_6]$ RTILs. In general, a class of cations will show glass transition temperatures around a similar temperature range (25,47,48). Here, the glass transition temperature is around -80 °C and is close to that for other imidazolium-based RTILs (45). A glass transition requires cation and anion reorganization to produce a more ordered material. The addition of CH_2 groups to the alkyl chain may require a minimal amount of additional thermal energy to produce the transition, hence the similarity in these results. Melting points, on the other hand, are not observed for $[\text{C}_6\text{mim}][\text{PF}_6]$ and $[\text{C}_8\text{mim}][\text{PF}_6]$, further supporting the observed tendency for RTILs to supercool.

When designing a RTIL, fine-tuning the properties can be achieved by changing the cation substituent groups, anion identity, or by mixing two types of RTILs with differing, but defined characteristics. For example, the combination of a TSIL with $[C_4mim][PF_6]$ can be used for Hg^{2+} and Cd^{2+} extraction (6). Incorporating anions to produce hydrophilic RTILs illustrates a wider range of properties, as shown in Table II. The effect of anion identity and, as a result, water content on the properties is obvious by comparison of Tables I-III.

Recently, we have prepared a series of RTILs containing 1-alkyl-isoquinolinium cations, combined with the bis(perfluoroethylsulfonyl)imide ($N(SO_2CF_2CF_3)_2$, [BETI]) anion, to produce a new class of ILs. We have also pursued their characterization and use in separations (26). The physical properties for $[C_nisoq][BETI]$ are summarized in Table IV.

Table IV. Properties of Water-Equilibrated $[C_nisoq][BETI]$ ILs (26)

<i>n</i>	Water Content (ppm)	Melting Point ($^{\circ}C$)	Glass Transition ($^{\circ}C$)
4	17700	-62.0	-85.2
6	16200	-77.3	-84.0
8	14900	-68.1	-79.4
10	6900	-59.3	-77.8
12	6600	-51.0	-75.4
14	6100	-49.7	-66.7
16	4700	-48.6	-61.8
18	4100	-47.2	-59.3

As the alkyl chain length ranges from butyl to octadecyl within this series, the hydrophobicity shows an order of magnitude increase. $[C_8isoq][BETI]$ and $[C_{14}isoq][BETI]$ were used in liquid-liquid partitioning experiments for a series of organic molecules (Figure 9) (26). Increasing the solute hydrophobicity (as denoted by the 1-octanol-water log *P* value produces increasing distribution ratios that are slightly higher in $[C_{14}isoq][BETI]$ compared to $[C_8isoq][BETI]$, congruent with the water content. In particular, the distribution ratios for 1,2,4-trichlorobenzene in $[C_{14}isoq][BETI]$ is 1280 (6100 ppm water) compared to 1130 in $[C_8isoq][BETI]$ (14900 ppm water). Using $[C_4mim][PF_6]$ (11700 ppm water) as the extracting phase, the distribution ratio is 524 (29).

Here, the composition of the IL makes significant contributions towards the partitioning results. Upon equilibration with water, $[C_{14}isoq][BETI]$ contains more water than water-equilibrated $[C_4mim][PF_6]$ (2), although the distribution ratios for 1,2,4-trichlorobenzene are much higher than in $[C_4mim][PF_6]$. It is not yet clear whether the extended aromatic region in $[C_{14}isoq]^+$ promotes interactions with aromatic solutes or if the observed trends are due to the extended hydrophobic environment offered by the longer alkyl chains.

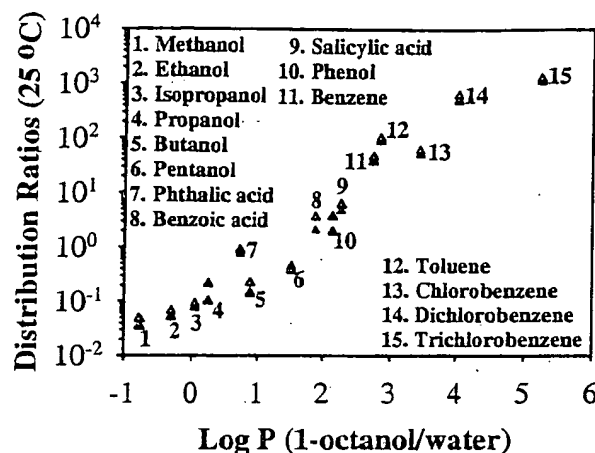


Figure 9. Distribution ratios for organic solutes from water to $[C_{8isoq}][BETI]$ (▲) or $[C_{14isoq}][BETI]$ (△) systems as a function of the solutes' 1-octanol-water log P values.

Crystal Structures

Since the scientific community has suggested an arbitrary 150 °C as an upper limit on "Ionic Liquid" melting points, there are many cation and anion combinations that produce crystalline materials that can be investigated to further understand the interactions in these systems. Parameters such as cation substitution and anion identity have been selected to investigate their contribution towards the solid state structure of ILs. Initial modeling studies focused on basic [1-methyl-3-ethylimidazolium][AlCl₄] systems and two models were proposed for the ionic structures; a stack model in which the anions were located between parallel planes of cations, or one in which Cl⁻ interacts with each hydrogen on the ring through hydrogen bonding (49,50). The crystal structure for [C₂mim][I] shows hydrogen bonding between the anion and the C-2 ring hydrogen (51).

For the [C_nmim][PF₆] ILs, the length of the alkyl chains and the ring substitution affects the solid state structure of the ILs. The crystal structure for [C₂mim][PF₆] has been reported (52) and we have obtained the crystal structure for [C₁₀mim][PF₆] (32). [C₁₀mim][PF₆], which melts at 38 °C and has been used in separations at elevated temperatures (3), has a unit cell where the cations are oriented in a bilayer arrangement. A similar arrangement has been observed for [C₁₂mim][PF₆] (24) where the cation structure also displays a noticeable, and yet unexplained, hook in the alkyl chain.

ILs display essentially 'salt-like' crystal packing in three dimensions for those cations containing short alkyl chains, while a restricted environment about the charged region is present in the bilayer structure for those with longer alkyl chains. The interactions are dominated by ion-ion coulombic interactions in PF₆⁻

structures and change with cation size. Thus, it appears that the key to designing ILs lies in understanding weak interactions that arise in addition to the coulombic interactions. By necessity, the cations and anions will orient themselves in a salt-like manner, but it is the interactions that result from packing frustration that are noticeable in the ILs.

As shown in Figure 10, the cation structures and lattice arrangements show a trend in charged vs. non-charged separations and hydrophobic packing in the structure. The crystal structure for the cation and packing diagram for [1-butyl-2,3-dimethylimidazolium][PF₆] is shown in 10a where no distinct regions of hydrophobicity are observed, owing to the length of the alkyl chain. Adding a methyl group to the C-2 in place of a hydrogen significantly increases the melting point of this IL, considering [C₄mim][PF₆] exists as a glass under practical conditions (2). Figure 10b shows the cation and unit cell for [C₁₀mim][PF₆]. As shown in the packing diagram, the bilayer arrangement dominates the structure, leaving a charge-rich region for the cation ring and anion to interact. Figure 10c shows the cation and lattice arrangement for [C₂mim][PF₆].

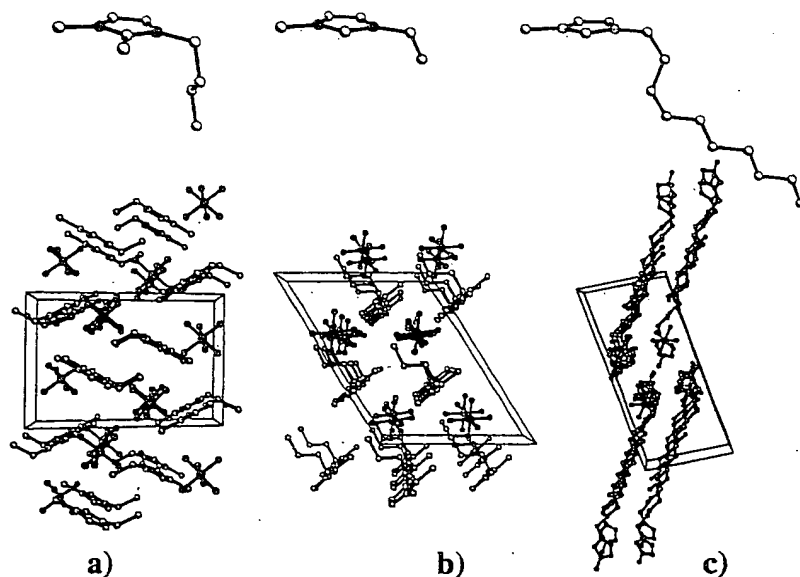


Figure 10. Cation and packing diagrams for three imidazolium-based PF₆⁻ ILs.

The alkyl chain length appears to have a significant influence on the solid-state structures for imidazolium-based ILs and results in two major types of orientations; salt-like and bilayer. Future solid-state analysis will facilitate the

understanding of ILs as to what cation and anion structural parameters contribute to stabilizing the resulting IL and the nature of the predominant interactions.

Conclusions

For separations, challenges lie in understanding the partitioning results with regards to those from more traditional systems. Continued study of organic solute behavior in RTIL-based liquid-liquid separations may facilitate a molecular level understanding of the partitioning mechanisms for neutral and ionic solutes, ultimately providing a predictive tool for their behavior. Exploring the driving forces for organic solute partitioning will contribute to the understanding of metal ion extractants, partitioning mechanisms in RTIL systems, and allow incorporation of new concepts such as Task Specific Ionic Liquids for separations.

Beyond the applications of ILs in liquid-liquid systems, the assortment of available and potential hydrophobic and hydrophilic RTILs attests to their easily manipulated physical properties. Through careful selection of cations and anions, significant or subtle changes can be made to the water content and rheological properties of the resulting RTILs. Indeed, crystallographic analyses indicate the structures of ILs result from several types of interactions which depend on the cation substitution and anion type.

The burgeoning field of IL research is producing exciting results and continues to demonstrate the potential for ILs in a variety of applications. Especially from the "Green Chemistry" standpoint, the chemical and physical properties of ILs, combined with their demonstrated utility as solvent replacements, warrants further study and exploration. Thus, the number of new and exciting examples of IL implementation in separations schemes is limited to time and the imagination.

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